EMPIRICAL TUNING METHODOLOGY FOR As AND Cl DOPING OF MOCVD GROWN CdTe

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ABSTRACT: Photovoltaic solar cells based on CdTe absorbers are still showing comparitively high efficiencies, currently at 16.5%. However, these cells rely on $CdCl_2$ treatments which are not fully understood and constrain flexibility over cell design. In this work, the effect of controlled arsenic and chlorine doping will be discussed as a potential alternative to $CdCl_2$ treatments. The CdTe/CdS structures were grown by MOCVD onto commercial ITO/glass substrates. Numerous growth and post-growth parameters were varied such as; the II:VI precursor ratios, the substrate temperatures (T_{sub}) and the *in situ* post-growth annealing ambient gas (H_2 or N_2). A strategic statistical design of experiments, the Taguchi matrix method, was used, to establish the best combination of material parameters for photovoltaic solar cell. High arsenic doping concentrations were needed to achieve a good photo-response in the test cells with a $J_{sc} = 24.3$ mA.cm^{-2}, but the cell efficiency was limited by other parameters $V_{oc} = 0.55$ V; FF = 40.9 %. The other main parameters increasing the cell efficiency were the *in situ* $CdCl_2$ treatment and substrate temperatures of 315°C and 390°C during the growth of CdS and CdTe respectively. Any post-growth annealing at 500°C damaged considerably the photocurrent response. The method has been successful in showing rapid progress with a new approach, using 16 material and process parameters, in just 36 experiments, for achieving acceptable PV test cells.

Keywords: CdTe, CdS, Doping, Experimental Methods.

1 INTRODUCTION

With a direct band gap of ~1.5 eV, CdTe is prone to be an ideal solar cell absorber material. Recent researches showed an increase in device efficiencies with 16.5 % for a Cu-based back contact [1] and 15.8 % using a Sb_2Te_3 back contact [2]. In both cases, the use of wet processes, high deposition temperatures (> 500 ^{o}C) and $CdCl_2$ treatments are aspects of the processing that deserve further attention as the production of CdTe solar cells goes to larger production scale.

It was previously demonstrated [3] that Arsenic doping as high as 2 x 10^{18} atoms.cm^{-3} could be substituted for Te into CdTe layers grown by Metal Organic Chemical Vapour Deposition (MOCVD) to enhance its p-type conductivity. The MOCVD technique gives the opportunity for greater control over material properties; however a systematic investigation of a large number of parameters is required. The flexibility and repeatability of the MOCVD technique have already been demonstrated through other area of optoelectronic devices.

2 EXPERIMENTAL METHODOLOGY

The CdS/CdTe structures were grown at atmospheric pressure, by MOCVD, in a horizontal reactor. The metal organic precursors were Dimethylcadmium (DMCd) for Cd, Diisopropyltelluride (DIPTe) for Te and for S, Ditertiarybutylsulphide (DTBS) were used. Hydrogen was used as a carrier gas during the growth of the layers. The substrates were commercially available ITO/glass, from Merck (soda lime) and Delta Technologies (alumino silicate). For the *in situ* arsenic doping in the CdTe layers, Tris-Dimethylaminoarsine (TDMAAs) was used in a double dilution line arrangement to ensure a stable molar flow while keeping a low partial pressure compared to those of DMCd and DIPTe. The n-Hexylchloride (n-HexCl) precursor was used in two ways:

- A direct *in situ* dopant, using 2 sccm in the line for CdTe and 10 sccm for CdS,
- An *in situ* post-growth treatment to grow $CdCl_2$ cap layer. The Cd:Cl precursor ratio was kept at 2.5.

In all cases, the as-grown layer thicknesses were monitored in real-time by a novel *in situ* triple wavelength interferometer. The three lasers, guided by fibre optics, operate at wavelengths of 532 nm, 635 nm and 980 nm, to keep a high accuracy of the layer thickness throughout the growth. The pre-cleaning of the substrates was found [4] to be a crucial step for a uniform coverage and adhesion of the structure. For the J-V characterisation of the cells, the light source of the instrument was composed of 4 x 60 W halogens providing a uniform power over the studied area (100 mW.cm^{-2}).

As can be seen in Fig. 1, various parameters had to be explored during the MOCVD process such as the II:VI ratios, doping levels, substrate temperatures (T_{sub}) and layer thicknesses (t_{CdS}, t_{CdTe}). For each possible parameter, a set number of levels have been attributed (i.e. numbers in brackets in Fig. 1) resulting in a finite and large number of possible combinations (i.e. 1,382,400). If all growth experiments were carried out, it would take 230 growth runs per year for 6,010 years! A different approach was needed.

The Taguchi method was selected for its capability of coping with a large parameter space and achieving convergence with a relatively small number of experiments [5]. Such strategic statistical approach is commonly used in the semiconductor industry to rapidly improve process robustness.

2.1 The glass substrate

For the glass type, the effect of Na diffusion was investigated by using two types of commercial ITO coated glass (Rs ~ 10 – 15 Ω/□). The most commonly used glass type is soda lime because of its low cost. However, the alumino silicate glass is also available, at higher cost, but avoids the contamination with sodium. If

the uncontrolled Na diffusion could be avoided, it would be beneficial for both understanding the relationship between materials purity with device performance and achieving more efficient devices.

2.2 The Window layer - CdS

The layer thickness, t_{CdS}, was varied from 120 to 350 nm to investigate its effect on optical transmission, pinholes and V_{oc}. The II:VI ratio (0.76 – 1.5) as well as T_{sub} (300 – 330 ^oC) were explored and had the potential to vary the grain size in order to act as a template for the CdTe layer. Increasing the point defects, with a Cd-rich CdS layer, was also investigated for chlorine doping and improvement of the photocurrent. Annealing at 450^oC and a Te buffer layer were explored in an effort to reduce the dislocation defects and stress at the interface arising from the lattice mismatch between the CdS and CdTe.
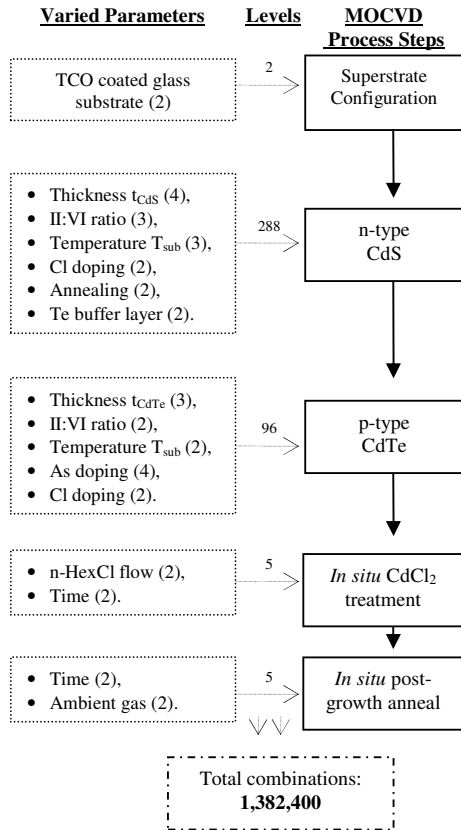

Figure 1: Schematic showing the different parameters for each process step during the MOCVD deposition of CdTe-based solar cell devices. The proposed level of parameter variations (number in brackets) would normally result in a large number of growth experiments which would be impossible to achieve in a life time.

2.3 The Absorber layer - CdTe

The absorber layer thickness, t_{CdTe}, was varied (2 – 6 μm) to achieve the optimum light absorption and electrical properties of the MOCVD grown CdTe. A Cd-rich CdTe layer was investigated to influence the point defects and affect the incorporation of both As and Cl doping. The deposition temperature, T_{sub}, was increased from 350^oC to 390^oC in an attempt to enlarge the CdTe

grain size and promote some intermixing at the CdS/CdTe interface.

2.4 In situ CdCl$_2$ treatment

To the authors' knowledge, *in situ* CdCl$_2$ anneal by MOCVD has never been reported. If successful, MOCVD could be a route for a one-step production scale process. In an attempt to verify its feasibility, the partial pressure of DMCd and n-HexCl, as well as the exposure time, were varied to confirm Cl diffusion into the CdTe.

2.5 In situ post growth annealing at 500^oC

Annealing was performed in the MOCVD reactor, varying the exposition time (10 – 30 mins) and ambient gas (H$_2$ or N$_2$) to promote the coalescence of grains and intermixing at the CdS/CdTe interface.

3 EXPERIMENTAL RESULTS WITH TAGUCHI METHOD

The growth experiments were clustered to avoid a large matrix of experiments and to promote smaller stages where each stage will establish a new set of optimum conditions. Four matrices were designed; one with 12 levels and three with 8 levels, where the number of growth experiments was reduced from 1,382,400 to 36! The method relies on a fundamental stability of the process selected. It was observed that the MOCVD grown devices were consistent in their characteristics but showed low efficiency without the post growth CdCl$_2$ anneal, in agreement with other deposition techniques.

The highest efficiency devices [1,2] also have a thin copper layer on the back surface to form a copper telluride contact. In this research the approach was taken to explore a different set of growth and device fabrication conditions that might give high efficiency devices. For the purposes of this study the back contacts were formed by Br/MeOH etch (0.25%) and 10 Au contacts (2.5 mm^2) were evaporated to check the uniformity of the J-V results. Some annealed at 400^oC and NP etched samples, gave higher efficiency, and will be published elsewhere, but the Br/MeOH was more consistent and therefore more suited to the Taguchi method.

3.1 Example of a Taguchi matrix analysis

Table I shows the design of the 3rd Taguchi matrix. In this example, the Taguchi results (T_i) (bottom row on Table I) are based on:
- Average efficiency results (η_j) for each run (j) (far right column on Table I),
- (-) & (+) combinations of levels (L_{ij}) for each parameter (i) and each run (j); where (-) is the starting value and (+) is the new value.

Mathematically, it can be written as follow:

$$T_i = \sum_j \eta_j \times L_{ij} \qquad (1)$$

Each Taguchi result was calculated, using Equ. (1), for each parameter. If the Taguchi result is negative, the new parameter value worsens the process, and vice versa if the value is positive. The higher the value of the Taguchi result, the more dominant the parameter is.

Taking the example of varying the substrate temperature, during the CdS growth, from 300°C to 330°C, an increase to 330°C had a negative effect on the cell efficiency according to the Taguchi result (T_i = -1.48).

The J-V characterisation of the grown devices allowed the best parameters to be explored based on the usual solar cell performances (i.e. η, J_{sc}, V_{oc}, FF). Each growth run is a combination of the parameter values and no two growth runs are the same in a given matrix.

Run	CdS T_{sub} (°C)	CdS II:VI	CdS T_{sub} / II:VI	t_{CdS} (nm)	t_{CdTe} (μm)	CdTe T_{sub} (°C)	As dope (p.p. / x10^{-7} atm)	η (%)
	(-) : 300 (+): 330	(-) : 0.76 (+): 1		(-) : 240 (+): 350	(-) : 4 (+): 6	(-) : 350 (+): 390	(-) : 4 (+): 8	
55	-	-	-	-	-	-	-	4.26
56	-	-	-	+	+	+	+	3.49
57	-	+	+	-	-	+	+	6.07
58	-	+	+	+	+	-	-	3.43
59	+	-	+	-	+	+	-	2.83
60	+	-	+	+	-	+	-	5.4
61	+	+	-	-	+	+	+	4.73
62	+	+	-	+	-	-	+	2.81
T_i	-1.48	1.06	2.44	-2.76	-4.06	6.36	-2.62	

Table I: The 3rd Taguchi matrix, demonstrating the working principle based on the results of device efficiency. (-) shows the starting and (+) shows the new values of a parameter. (note: p.p. means partial pressure).

3.2 Starting point for the MOCVD PV devices

The starting point was to grow a CdS/CdTe structure with the simplest set of parameters previously used to produce MOCVD grown structures for *ex situ* CdCl$_2$ treatments [6]. The combination of parameters, shown in Table II, gave measured devices with an efficiency of 0.1%.

CdS	T_{sub} (°C)	300
	II:VI	0.76
	t_{CdS} (nm)	120
CdTe	T_{sub} (°C)	350
	II:VI	1
	t_{CdTe} (μm)	2
	Doping	None
Annealing		None

Table II: Starting values of the parameters for the MOCVD grown CdS/CdTe structures.

3.3 The 1st Taguchi matrix

The first Taguchi matrix investigated some of these starting parameters (see Table II), including the introduction of doping into the CdTe layer and *in situ* CdCl$_2$ treatment, as well as *in situ* post growth annealing. At this stage it was not clear what interactions would occur, such as between Cl doping and annealing, so a 12 levels matrix was chosen to allow for possible interactions. Two levels were chosen for each of the selected parameters (see Table III).

t_{CdS} (nm)	t_{CdTe} (μm)	As dope in CdTe (p.p. / x10^{-7} atm)	Cl dope in CdTe (flow / sccm)	In situ CdCl$_2$ treatment (mins)	In situ Post growth anneal (30 mins) (°C)
(-) : 120 (+): 240	(-) : 2 (+): 4	(-) : None (+): 4	(-) : None (+): 2	(-) : None (+): 10	(-) : None (+): 500
-1.06	6.2	6.28	0.86	-6.32	1.2

Table III: Selected parameters to be explored and their Taguchi results (T_i) for the 1st Taguchi matrix.

The biggest positive change was As doping with a concentration of 3×10^{17} atoms.cm^{-3}, verified by quantitative SIMS [7]. The thicker CdTe also made a positive contribution to the efficiency. The annealing at 500°C for 30 minutes had a dramatic effect on decreasing the efficiency. As all interactions in the matrix related to the annealing, there relevance was somewhat diminished. The annealing did enhance the coalescence of the grains but it also promoted the diffusion of Na and S into the CdTe layer, confirmed by SIMS [7], which consequently destroyed the CdS/CdTe interface. The best average efficiencies were measured for the following growth runs:

- SGEN12: η = 2.25 ± 1.47 %
- SGEN15: η = 2.56 ± 0.13 %

3.4 The 2nd Taguchi matrix

The parameters of SGEN15 were taken as the starting conditions of the 2nd Taguchi Matrix. SGEN25 gave η = 1.84 ± 0.73 %, agreeing with both SGEN12 and SGEN15 within experimental error. The selected parameters varied for this matrix are listed in Table IV.

As dope in CdTe (p.p. / x10^{-7} atm)	CdTe II:VI	CdTe II:VI / As doping	Substrate type	In situ CdCl$_2$ treatment (time / mins)	In situ Post growth anneal at 500°C (mins)
(-) : 4 (+): 0.8	(-) : 1 (+): 1.75		(-) : S. (+): A.	(-) : 10 (+): 45	(-) : 30 (+): 10
-0.29	0.63	1.05	0.73	1.03	-10.37

Table IV: Selected parameters to be explored and their Taguchi results (T_i) for the 2nd Taguchi matrix. For the substrate type, "S." means soda lime and "A." means alumino silicate.

The main positive parameters were a longer *in situ* CdCl$_2$ treatment and the new alumino silicate glass substrate. The interactions between the CdTe II:VI ratio and the As doping, revealed that a Cd-rich CdTe and a higher partial pressures of As resulted in an increased constant concentration level of 3×10^{18} atoms.cm^{-3} throughout the CdTe layer. The worst parameter, for the efficiency, was found to be the annealing again despite reducing the exposition time. To confirm that the ambient gas was not the main cause of the degradation during *in situ* annealing at 500°C, both annealing in H$_2$ and N$_2$ were carried out at this point and confirmed that the temperature alone was the main cause. This parameter was discarded for any subsequent matrix. The best device was from SGEN29 with an average efficiency of 2.79 ± 0.33 %.

3.5 The 3rd Taguchi matrix

Despite being the main parameter for efficiency improvement in the 2nd Taguchi matrix, the CdCl$_2$ treatment was put on hold to concentrate on the further investigation of As doping into the CdTe layer. The 3rd Taguchi matrix is shown in Table I.

The starting conditions of the 3rd Taguchi matrix were based on SGEN29 but without CdCl$_2$ treatment. The average efficiency from the first growth run, SGEN55, was in agreement with SGEN29 but with a slight increase (i.e. η = 4.26 ± 0.32 %). This increase may be attributed to both the lack of CdCl$_2$ treatment and a slight loss of light calibration of the J-V instrument.

Increasing the substrate temperature to 390°C during the CdTe growth and changing the CdS II:VI to 1,

represented the main positive aspects of cell efficiency improvement. Increasing the deposition temperature during the CdTe growth also had a positive effect on improving the V_{oc}.

Increasing the thickness of both the CdS and CdTe, as well as increasing T_{sub} during the CdS growth gave negative results for the efficiency. However, when looking at the interaction between the CdS II:VI and T_{sub}, seems to indicate that either $T_{sub} = 330^{o}C$; II:VI = 0.76 or $T_{sub} = 300^{o}C$; II:VI = 1 would be advantageous for the cell's efficiency. The best efficiency of 6.07 ± 0.40 % was achieved with SGEN57.

3.6 The 4th Taguchi matrix

In an effort to further investigate the performance of the CdS window layer and CdS/CdTe interface, the parameters of the 4th Taguchi matrix were selected, as seen in Table V.

The efficiency measured for SGEN57 was not reproduced here as SGEN65 only gave an average efficiency of 4.60 ± 0.24 %. The most likely reason is that the CdTe growth was interrupted for SGEN57 and could have contributed to the efficiency shift.

The positive and negative outcomes of this matrix were not as pronounced as the other matrices which would lead to believe that the selected parameters had a lower effect on the average efficiency. The main positive changes are the increase to $315^{o}C$ of T_{sub} during the CdS growth and the CdS annealing at $450^{o}C$. A Cd-rich CdS and chlorine doping had the worth negative effect on the efficiency. SGEN71 gave the best efficiency of this matrix with $\eta = 4.65 \pm 0.30$ %

CdS T_{sub} (°C)	CdS II:VI	CdS T_{sub} / II:VI	T_{CdS} (nm)	CdS annealing at 450°C (mins)	Te layer at 390°C (mins)	Cl dope in CdS (flow / sccm)
(-) : 300 (+): 315	(-) : 1 (+): 1.5		(-) : 240 (+): 180	(-) : None (+): 5	(-) : None (+): 10	(-) : 0 (+): 10
0.94	-1.66	-0.54	-0.6	0.48	0.32	-1.44

Table V: Selected parameters to be varied and their Taguchi results (T_i) for the 4th Taguchi matrix.

3.6 Summary on the experimental results

The overall efficiency of the devices presented here has significantly improved by implementing the Taguchi matrix method. This statistical approach has enabled us to concentrate on step changes and investigate a wide range of parameters with relatively few growth runs. Fig. 2 clearly shows the increase in efficiency and the improved repeatability and reproducibility of the average efficiencies.
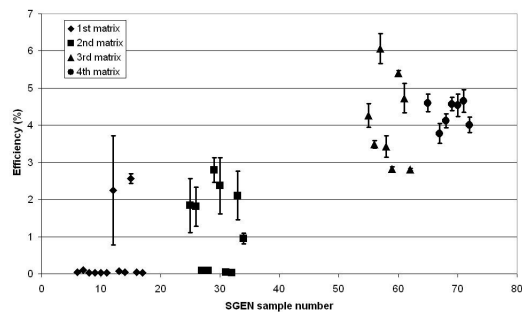

Figure 2: Plot of the average cell efficiencies for each growth run of the 4 Taguchi matrices. A net efficiency

improvement and reduced variance in efficiency is clearly visible.

6 CONCLUSION

It was shown that using a design of experiment method such as the Taguchi matrix enabled parameters to be explored efficiently by developing set of experiments. The main parameters affecting certain aspects of the grown cell can easily be extracted from the Taguchi matrices. In the case of the cell efficiency, the main parameters have been listed in Table VI.

In order to use the Taguchi method correctly, a reliable deposition process is needed, and the MOCVD process has shown to be perfectly suited for the task.

A photovoltaic solar cell efficiency of 6% was achieved, without $CdCl_2$ treatment, growing an As doped Cd-rich CdTe absorber at 390°C (J_{sc} = 24.3 mA.cm^{-2}; V_{oc} = 0.55 V; FF = 40.9 %). Good J_{sc} have been achieved so far with the introduction of Arsenic doping, however, V_{oc} needs to be higher to achieve higher efficiencies and this will be the next focus for the upcoming Taguchi matrices. It is worth noting that when similar samples were annealed at $400^{o}C$ and NP etched, the average efficiency increase above the 8% threshold.

Taguchi matrix	Main parameters affecting the MOCVD devices Efficiency	
	With a positive effect	With a negative effect
1	Arsenic doping	Long annealing at 500°C
2	*in situ* CdCl$_2$ treatment	Short annealing at 500°C
3	T_{sub} at 390°C during CdTe growth	t_{CdTe} increased to 6µm
4	T_{sub} at 315°C during CdS growth	Cd-rich CdS layer

Table VI: Summary of the main parameters affecting the device efficiency retrieved from each Taguchi Matrix.

7 ACKNOWLEDGEMENTS

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